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LASER INDUCED LUMINESCENCE OF MILITARY TARGETS.(U)
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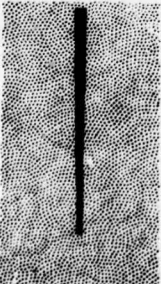


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LASER INDUCED LUMINESCENCE OF MILITARY TARGETS

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Research Directorate
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1. INTRODUCTION

The objective of this report is to identify specific problem areas where laser induced luminescence may prove useful to current Army remote sensing systems and terminal homing devices. Luminescence, as any other molecular emission process (e.g., Raman emission), is typical of a particular molecular system and should provide the basis for discrimination of a given target if sufficient spectral resolution is employed. The military applications of laser induced luminescence and the conditions under which the return luminescence signal can be put to best use are discussed in this report.

In particular we concentrate on the possibility of exciting luminescence in camouflaging pigments or dyes of military targets, such as tanks. A laser designator beam used for terminal homing in missile systems could induce luminescence in the target paint. Since this luminescence is characteristic of the target it could be used to discriminate the target from the background.

It is well known that the main task of camouflaging materials is to reduce the detectability of military targets by blending the spectral response of the dyes or pigments with that of the surrounding background. A truly effective camouflaging dye should match the spectral reflectance of the background over the entire spectral range available to ordinary surveillance devices. In practice, as well as in principle, this cannot be accomplished with complete success because different molecular structures can be made to respond differently if one uses suitable illumination schemes.

Thus, selective excitation of chlorophyll and camouflaging dyes by laser radiation has been seen to produce significantly different emission spectra. In practice, this implies that even a camouflaging material will eventually stand out against the background if the constituent molecules are selectively excited to a higher internal energy level and allowed to relax to the ground state by luminescent emission. (This process can be quenched, sometimes rather effectively, by appropriate engineering of the molecular structures, such that the intersystem crossing to the long lived triplet states is enhanced.)

It appears that a sensible question to ask should be the following: Can we make the luminescence return signal specific enough to serve as an effective friend or foe identification device?

There are two routes one may follow in exploring this question: One may look for specific signatures emitted by enemy camouflaging materials, or, alternatively, one may enhance

certain luminescence features of friendly camouflaging dyes. Such features should not be permanent for obvious reasons of security. A particular signature could be coded to correspond to a particular mission, and then replaced with another one, depending on the need.

The latter choice appears to be more practical and more in line with certain additional requirements of current surveillance schemes for the following reasons. Reported luminescence measurements of military uniforms and camouflaging materials have indicated fairly similar responses from friendly and enemy uniforms. Most dye molecules fluoresce strongly with a measurable output at significant distances. The spectral output is broad and makes friend and foe discrimination difficult to perform in a highly specific way. It appears difficult to design a surveillance system whose task is to sort out broad spectral features, and to correlate them with the expected returns from numerous enemy fabrics and camouflage materials.

On the other hand, if appropriate modifications are introduced in the dye molecules used in friendly camouflaging materials, it may be possible to elicit a highly specific response that will enable positive identification of friendly personnel. It is desirable to perform surveillance using infrared laser systems such as Nd-YAG lasers. Most dye molecules have a limited luminescence yield when irradiated with IR radiation. It seems possible, however, to engineer dye molecules such that a strong absorption band would be located in the IR region of operation of commonly used surveillance lasers. Such dyes could be used in friendly camouflaging materials and the luminescence signal used for highly specific identification purposes. In this case remote monitoring of field activities could be accomplished by conventional techniques and supplemented by IR luminescence systems. These considerations indicate the desirability of pursuing a systematic analysis of laser induced luminescence for the purpose of providing a highly specific detection system of friendly units.

The absorption of electromagnetic radiation by large organic molecules is often followed by rapid (10 to 100 μ sec) molecular de-excitation and emission of light (luminescence). Luminescence spectra are red-shifted relative to the frequency of the exciting radiation. Furthermore, the luminescence yield (i.e., the ratio between the emitted and the exciting electromagnetic energy per molecule) can be substantially smaller than unity due to internal conversion processes which tend to distribute the absorbed energy among numerous degrees of freedom. The processes that give rise to luminescence are discussed in Section 3. Since Army surveillance and remote detection systems usually employ near-infrared or infrared lasers, in Section 4 we have investigated the expected requirements that a dye molecule should

satisfy in order to have a fundamental absorption band around $1\ \mu\text{m}$ and a strong fluorescence emission. We also discuss a simple, but often quantitatively accurate, model for correlating structural changes in chain-like molecular dyes and their fundamental absorption band.

On the basis of a literature search on the state-of-the-art technology in the area of remote optical monitoring, discussed in the next section, and especially of atmospheric pollution detection, we conclude that there is no difficulty, in principle, with the excitation and detection of luminescence by conventional CW or pulsed visible lasers over moderately long ranges (several hundreds of meters to a few kilometers).^{1,2}

2. A SURVEY OF CURRENT APPROACHES TO REMOTE OPTICAL MONITORING

There is a good deal of similarity between the objectives and techniques employed in remote optical monitoring and the proposed laser excitation and detection of luminescence from molecules. Remote optical monitoring with a CW or a pulsed laser is an important problem area with significant payoffs in many branches of scientific, industrial, and environmental concern. The need for remote sensing of the chemical pollutants in the atmosphere, for example, is perhaps one of the best publicized recent areas of investigation.³ Invariably, the success of remote sensing techniques is based on our ability to detect signatures of molecular species which will provide means for rapid quantitative analysis with high specificity and sensitivity.

Four partially complementary approaches are widely used:

- **ABSORPTION.**^{4,5} The laser is fine-tuned across a strong absorption line of a given molecular species, and the transmitted beam is detected either by a remote detector or with the

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1. J. A. Sousa, J. F. Roach, E. F. Wyner, M. Nakashima and R. Grojean, *Laser-Induced Luminescence Studies (I) Remote Detectability under CW Radiation*, US Army Natick Laboratories, Natick, Massachusetts (February 1973). (Unclassified).
 2. J. A. Sousa, J. F. Roach, M. Nakashima, E. F. Wyner, J. Weinstein, R. C. Clapp and R. Grojean, *Laser-Induced Luminescence Studies*, US Army Natick Laboratories, Natick, Massachusetts (June 1974). (Unclassified).
 3. F. F. Hall in *Laser Applications*, Vol. 2, Academic Press, New York, (1974) p. 161.
 4. R. T. Ku, E. D. Hinkley and J. O. Sample, *Applied Optics* 14, 854 (1975).
 5. P. L. Kelly, R. A. McClatchey, R. K. Long and A. Snelson, *Optical Quantum Electronics* 8, 177 (1976).

help of a retroreflector. The latter scheme allows the transmitting and receiving stations to be located in the general vicinity of one another. These measurements have the highest sensitivity and do not require large laser power. On the other hand, the received information provides no depth resolution.

- **LASER RAMAN.**^{6,7,8} This method requires a pulsed laser of high intensity and fixed frequency to produce the backscattered Raman signal. The downshifted nature of the Raman line leads to a natural, although not necessarily trivial, discrimination of the signal of interest from the unshifted Mie and Rayleigh backscattered components. One of the attractive advantages of the technique is that a multicomponent gas mixture can be analyzed by direct identification of well known Stokes Raman molecular lines. Furthermore, a concentration calibration scheme is automatically available in the ever present O₂ and N₂ reference Raman lines. The success of this method depends, to a large extent, on the availability of stable intense laser sources. On the other hand, the scattered signal can be enhanced by tuning the source on an absorption band of the molecular system to be analyzed (resonance Raman effect). Techniques have also been developed for correcting the effects of pulse to pulse fluctuations and local atmospheric variations.

- **RESONANCE BACKSCATTERING.**^{9,10} The laser is tuned to a strong transition of a molecular species. The selective excitation is followed by broad-banded and red-shifted resonance fluorescence which can be detected in the backscattered signal.

- **REMOTE HETERODYNE DETECTION.**¹¹ This technique is used for the detection of characteristic emission, rather than absorption, lines from hot sources such as the exhaust plumes of jet engines. A semiconductor laser is tuned to the emission line of a hot gas. The existence of the beat signal provides direct evidence for the presence of a given atomic or molecular species, while the signal amplitude gives a relative measure of the molecular concentration.

6. L. R. Lidholt, *Opto Electronics* 4, 133 (1972).

7. T. Hirschfeld, *Applied Optics* 12, 1435, 1615 (1974).

8. D. A. Leonard, *Optical Quantum Electronics* 7, 197 (1975).

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10. J. A. Gellwachs, *Applied Optics* 12, 2812 (1973).

11. R. T. Menzies and M. S. Shumate, *Science*, 184, 570 (1974) and *Applied Optics* 15, 2080 (1976).

The successful demonstration of the main schemes adopted in remote monitoring indicates that, at least in principle, the state-of-the-art technology allows the long range detection of weak return signals with sufficient resolution and specificity for similar laser induced luminescence schemes to be feasible.

Before discussing some specific ideas related to our main task, it will be useful to survey the main physical processes which are responsible for luminescence in large organic dye molecules.

3. MOLECULAR RELAXATION PATHWAYS AND LUMINESCENCE

In this section we consider the main photophysical processes by which the excited molecule loses its energy.^{12,13} We exclude photoionization and the formation and destruction of chemical bonds from our discussion, since we are especially concerned with the main pathways leading to the emission of radiation from an excited molecular state.

The kinetic processes schematically shown in *Figure 1* apply to solutions or condensed phases of typically large organic molecules where the final radiative emission steps occur after thermalization of the excited singlet or triplet states. The absorption of pump radiation between the S_0 singlet ground state and the excited electronic states S_1 and S_2 occurs at the rate $\sigma_{ij}I$ where σ_{ij} is the absorption cross section for the $0 \rightarrow 1$ or $0 \rightarrow 2$ transitions and I is the incident flux of the pump. If the excited singlet state S_1 is populated, absorption of radiation can also occur between the states S_1 and S_2 . The excited molecular system usually reaches a condition of equilibrium between the vibrational states of the first and second excited electronic levels. The equilibration process is accompanied by internal conversion or intersystem crossing processes, which result in non-radiative decay, as well as in the formation of occupied triplet excited states. These, in turn, relax slowly to the ground singlet state by emission of phosphorescent radiation.

The radiative decay (luminescence) that is of interest for our task occurs directly from the excited singlet state either spontaneously or by stimulated emission by the pump pulse itself, if the incident flux is intense enough to compete with the rapid vibrational thermalization process.

12. G. W. Robinson in *Excited States*, E. C. Lim, Ed., Vol. 1, Academic Press, New York, (1974) p. 1.

13. B. R. Henry and W. Siebrand in *Organic Molecular Photophysics*, J. B. Birks, Ed. Vol. 1, Wiley, New York (1973) p. 153; Vol. 2 (1975), p. 303.

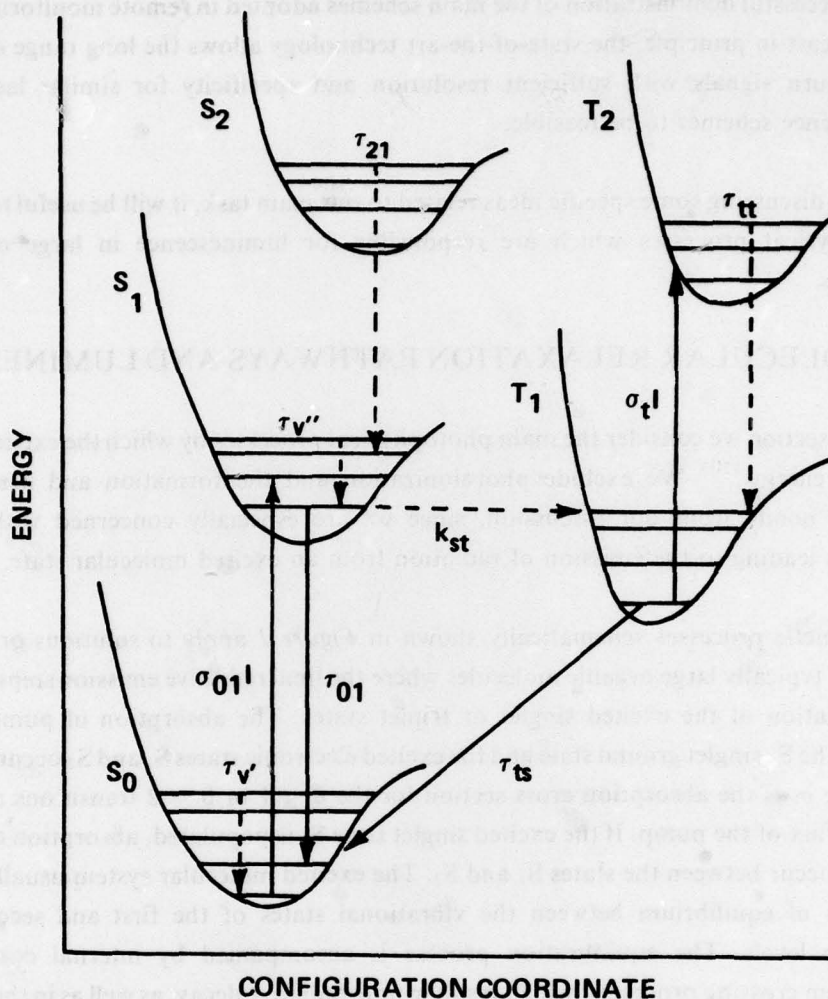


Figure 1. Schematic configuration diagram of a large organic molecule. The symbols S_i and T_i designate singlet and triplet states; $\sigma_{ij}I$ represents the absorption rates for transitions between states i and j induced by a pump of intensity I . The corresponding absorption rates in the triplet manifold are labeled σ_{Tj} . Typical decay processes illustrated in the figure are identified by their respective decay times.

$\tau_{v'}$	=	vibrational relaxation in the ground electronic level
$\tau_{v''}$	=	vibrational relaxation in the excited electronic level
τ_{01}	=	fluorescence decay
τ_{ts}	=	phosphorescence decay
τ_{21} or τ_{tt}	=	non-radiative internal conversion processes
k_{st}	=	intersystem crossing rate constant.

A competing mechanism which may cause a reduction of the luminescence quantum yield is the laser induced absorption process $S_1 \rightarrow S_2$.¹⁴ The result of the absorption causes the total fluorescence output from the $S_1 \rightarrow S_0$ transition to be intensity dependent. For moderate pump intensities the total fluorescence quantum yield ϕ is smaller than what one would measure if the absorption cross section were zero. Typically, the fluorescence yield will behave according to a Stern-Volmer type law

$$\phi/\phi_0 = \frac{1}{1 + \tau_{10}\sigma_{12}I}$$

where

ϕ_0 = the limiting fluorescence yield corresponding to low pump fluxes

σ_{12} = the absorption cross section for the $S_1 \rightarrow S_2$ transition

τ_{10} = the fluorescence decay time from S_1 to S_0 .

Interesting studies of ultrafast decay and competing processes have been performed in dye molecules.¹⁵ They will not be reviewed here because their relevance to military applications seems limited. Their main impact is at a more fundamental level in understanding the dynamics of the radiative and non-radiative processes that determine the ultimate available luminescence yield of a dye molecule.

4. LASER INDUCED LUMINESCENCE

For a successful implementation of a remote sensing system using laser induced luminescence the ideal dye molecule should be characterized by:

- A strong near-infrared absorption band;

14. J. T. Knutson and E. M. Eyring, *Journal of Physical Chemistry* 78, 2355 (1974).

15. A. Laubereau and W. Kaiser, *Opto Electronics* 6, 1 (1974).

- Small intersystem crossing rate (to insure limited amount of luminescence quenching by singlet-triplet transitions);

- Fairly narrow luminescence spectrum and high radiative yield.

Additional requirements to be imposed on the detection system are well known. They include an efficient collection optics, high gain detectors with a near-IR sensitive surface and electronic filtering to improve the ratio of the luminescence signal to the background noise even in the presence of daylight. These requirements are well within the state-of-the-art of remote sensing technology. Here we focus on some general guidelines for selecting a suitable dye with the specified properties.

The search for an appropriate dye molecule turns out to be a problem of concern also with regard to the design of infrared CW dye lasers. It is known that CW operation of a dye laser in the infrared can be achieved, at the present time, with polymethine dyes excited, for example, by the red line of a krypton laser. The approximate tuning range of these dyes covers the spectral range from about 7000 to 9500 Å. The possibility of extending the working range to about 1.1 μm is being considered actively.

Not only is the near-IR region of the spectrum important for studying optical communication materials, but the predicted conversion efficiency of these IR dye lasers is even higher than that of the Rhodamine 6G dye.

Polymethine molecules have a long, chain-like structure with conjugated double bonds along the chain (*Figure 2*). This structure allows the synthesis of a variety of derivatives which account for the large spectral lasing range covered by this dye. The length of the chain can be varied as shown schematically in *Figure 3*, and derivatives can be formed by modifications of the end groups X, R, W as well as by several substitutions at the center of the chain.

The direction in which one should be moving to engineer a dye molecule with the required spectral features can be mapped out qualitatively, and sometimes even quantitatively, using simple heuristic models. Clearly, an exact quantum mechanical description of these molecules is a forbidding task. However, as a first approximation the π -electrons of the conjugated double bonds can be considered as a one-dimensional free electron gas that spreads along the molecular chain. More precisely, a planar dye molecule such as the symmetrical polymethine shown in *Figure 2* is considered to be resonating between two limiting structures (a) and (b). The atoms that make up the chain have their centers in the plane and are joined by σ -bonds. Each carbon atom of the chain and the two nitrogen atoms at the ends are the centers of three

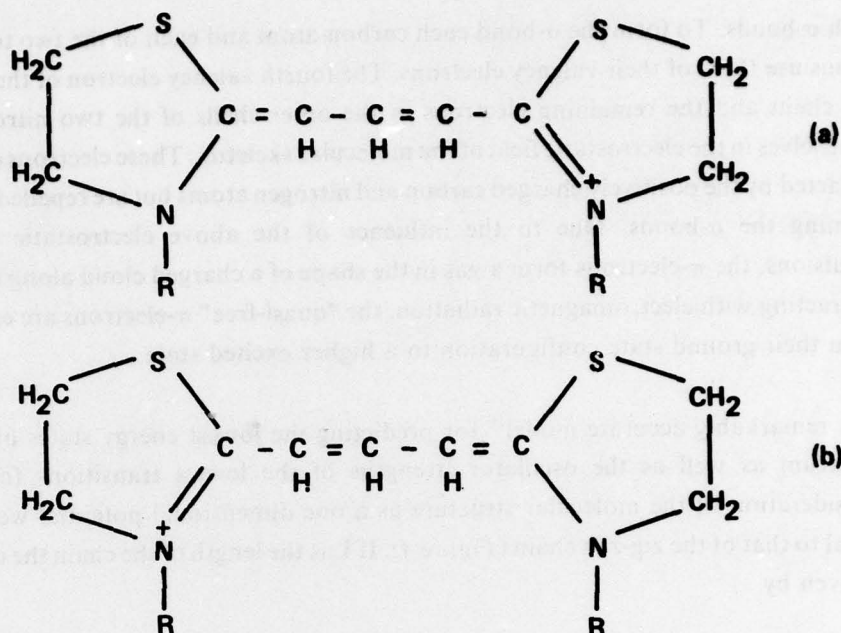


Figure 2. A simple example of symmetrical polymethine dye. The cation, which is responsible for the color, is considered to be resonating between two limiting structures (a) and (b), each making the same contribution to the normal state of the cation.

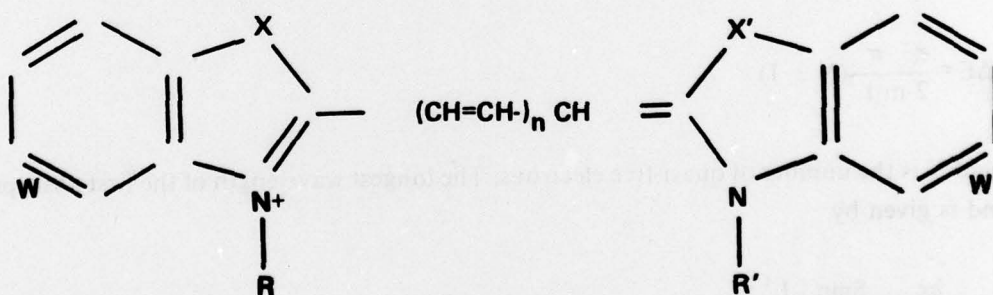


Figure 3. Schematic formula of polymethine dye. Length of chain n can be one to five elements. The locations where various groups can be substituted are indicated by W, X, R, and Z.

such σ -bonds. To form the σ -bond each carbon atom and each of the two terminal nitrogen atoms use three of their valency electrons. The fourth valency electron of the carbon atom in the chain and the remaining electrons in the outer shells of the two nitrogen atoms find themselves in the electrostatic field of the molecular skeleton. These electrons (π -electrons) are attracted by the positively charged carbon and nitrogen atoms but are repelled by the electrons forming the σ -bonds. Due to the influence of the above electrostatic attractions and repulsions, the π -electrons form a gas in the shape of a charged cloud along the chain. When interacting with electromagnetic radiation, the "quasi-free" π -electrons are easily transferred from their ground state configuration to a higher excited state.

A remarkably accurate model¹⁶ for predicting the lowest energy states of the π -electron spectrum as well as the oscillator strengths of the lowest transitions follows from the consideration of the molecular structure as a one dimensional potential well with a length equal to that of the zig-zag chain (Figure 4). If L is the length of the chain the energy spectrum is given by

$$E_n = \frac{\hbar^2 \pi^2}{2 m L^2} n^2.$$

Since, however, the lowest energy levels are occupied by the free electron gas, the first optical transition occurs when one of the electrons in the highest occupied state jumps to the lowest free level. Each level is occupied by no more than two π -electrons; therefore, the highest occupied level corresponds to $n = \text{Int } (N/2)$. The energy difference corresponding to the fundamental transition is given by

$$\Delta E = \frac{\hbar^2 \pi^2}{2 m L^2} (N + 1)$$

where N is the number of quasi-free electrons. The longest wavelength of the first absorption band is given by

$$\lambda_1 = \frac{hc}{\Delta E_1} = \frac{8mc}{h} \frac{L^2}{N + 1}.$$

The intensity of the absorption band, which is also proportional to the intensity of the luminescence emission, is measured by the oscillator strength $f_{A \rightarrow B}$ of the transition between

16. H. Kuhn, *The Journal of Chemical Physics* 17, 1198 (1969).

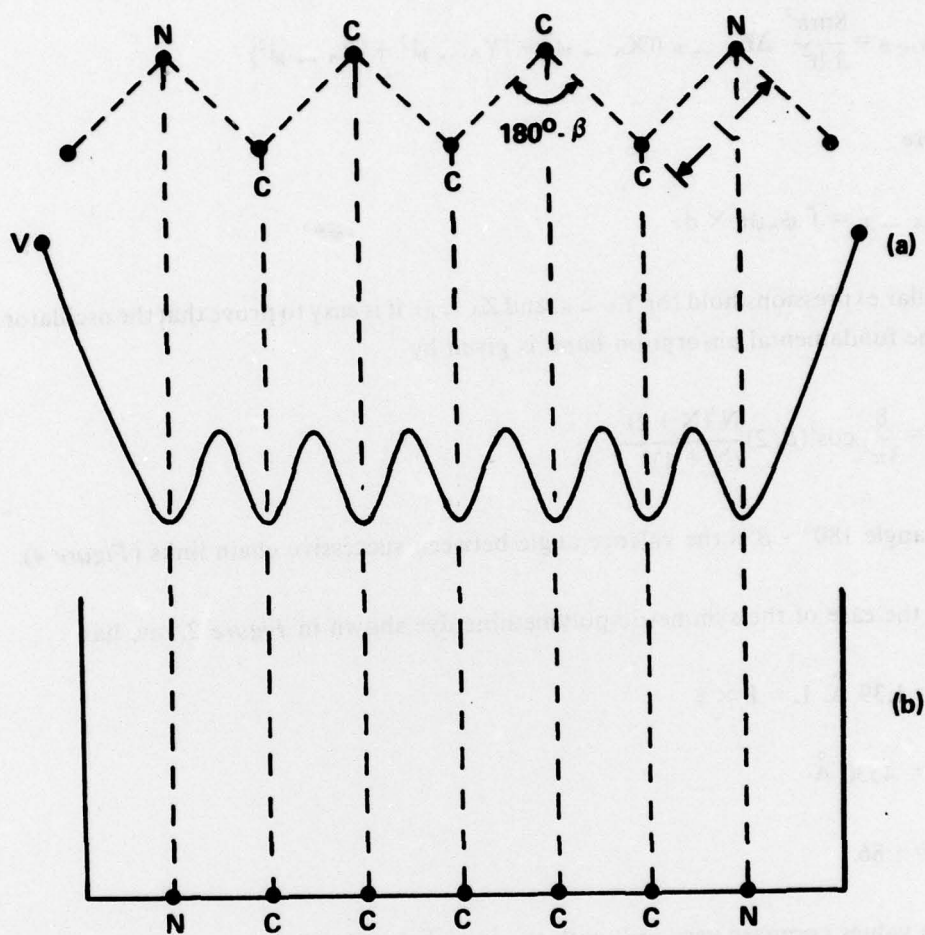


Figure 4. According to the model the π -electrons can only move along and in the direction of the polymethine zig-zag chain of length L . The qualitative potential energy (a) along the length L is replaced for a rough quantitative analysis by the square well (b).

the initial and final configurations (A and B, respectively). Since the oscillator strength is defined by

$$f_{A \rightarrow B} = \frac{8m\pi^2}{3h^2} \Delta E_{A \rightarrow B} (|X_{A \rightarrow B}|^2 + |Y_{A \rightarrow B}|^2 + |Z_{A \rightarrow B}|^2)$$

where

$$X_{A \rightarrow B} = \int \psi_A \psi_B^* \times d\tau$$

(similar expressions hold for $Y_{A \rightarrow B}$, and $Z_{A \rightarrow B}$), it is easy to prove that the oscillator strength of the fundamental absorption band is given by

$$f_1 = \frac{8}{3\pi^2} \cos^2(\beta/2) \frac{N^2(N+2)^2}{(N+1)^3}.$$

The angle $180^\circ - \beta$ is the valence angle between successive chain links (*Figure 4*).

In the case of the symmetric polymethine dye shown in *Figure 2*, one has

$$\ell = 1.39 \text{ \AA}, L = 8 \times \ell$$

$$\lambda_1 = 4530 \text{ \AA}$$

$$f_1 = 1.86.$$

These values compare very well with the experimental values

$$\lambda_{\text{EXP.}} = 4450 \text{ \AA}$$

$$f_1 = 1.2.$$

From the above simple minded model it is clear that an infrared absorption band requires lengthening of the rigid linear chain. In fact, increasing the chain length in symmetrical polymethine dyes with identical end groups by one carbocyanine group shifts the emission wavelength by about 1000 \AA into the infrared.¹⁷

17. K. M. Romanek and O. Hildebrand, *Laser Focus*, August (1977), p. 50.

"Fine tuning" of the dye molecule can be obtained by modification of the end groups, such that the walls in which the π -electrons are moving become less steep (this causes the separation of the energy levels to become smaller). It has been found, for example, that if an additional benzene group is attached to the end group at point W (*Figure 3*) the fundamental emission is red-shifted by about 500 Å, while exchanging an ethyl group for a methyl group at point R causes a shift of about 50 Å in the optical absorption curve.

In addition to the appropriate red-shift in the absorption band an important requirement for our purposes is to obtain the largest possible luminescence efficiency. Because the main cause of the efficiency loss in the emission is the absorption of the exciting radiation by triplet to triplet transition, the intersystem crossing rate should be kept as low as possible.

It is found that the yield of triplet formation in a dye increases if heavy atoms with their high spin-orbit coupling are in the vicinity of the axis of the dye molecule. Thus the four typical dye families listed as (a) through (d) in *Figure 5* have increasing intersystem crossing rates. Failure to obtain CW laser output from quinocarbocyanine (d) has been ascribed to the "short circuit" produced by the high spin-orbit coupling of the π -electron and the HC-CH group at point X.

In conclusion, to produce high yield luminescence from a dye with a fundamental absorption band around 1 μm , new dye molecules must be synthesized. Quinocarbocyanines have been noted to have an absorption band at about 1 μm but the luminescence yield is greatly reduced by the triplet quenching effect discussed above.

The best candidates for our purpose appear to be indo- or oxacarbocyanines with four or five carbocyanines groups. These long chains are chemically not very stable and rigidizing neopentylene rings must be built into the chain.¹⁷ The task of synthesizing a reasonably long and stable molecule appears to be the main present technical task. If achieved, one is expected to be able to push the emission spectrum of the dye molecules closer to its theoretical limit which is estimated to be about 1.3 μm .

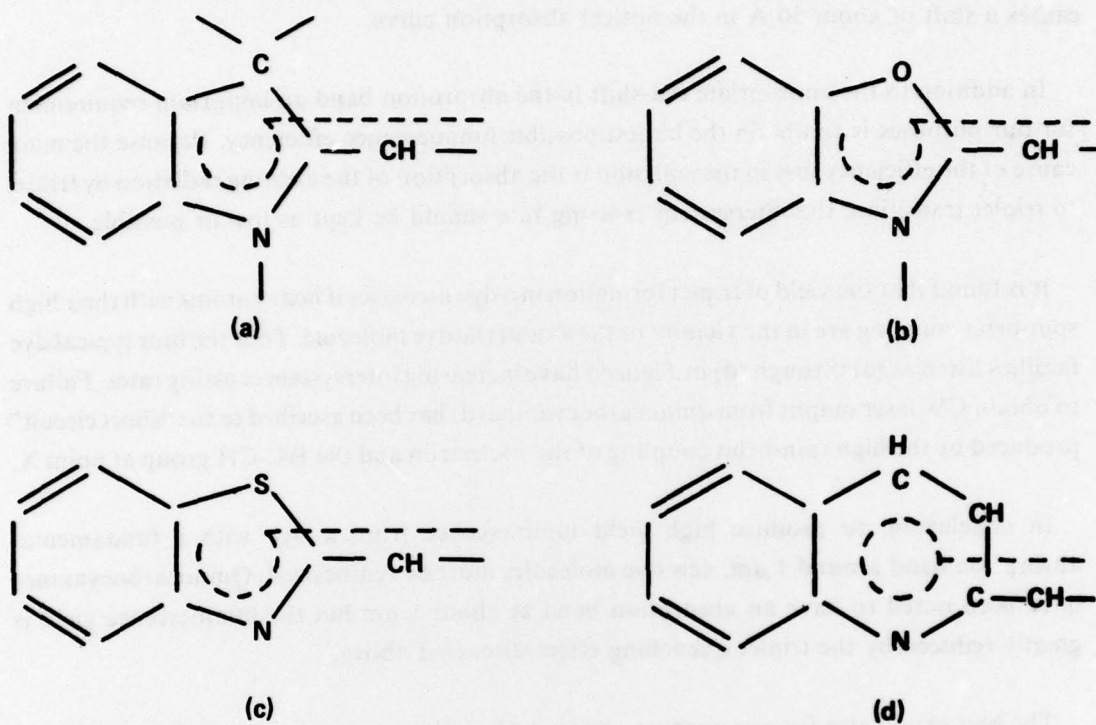


Figure 5. Common structures of end groups. Dots indicate π -electrons. Dye families are (a) indocarbocyanine, (b) oxacarbazocyanine, (c) thiocarbazocyanine and (d) quinocarbazocyanine.

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